

Heterospin complex showing spin transition at room temperature



S.E. Tolstikov^a, N.A. Artiukhova^a, G.V. Romanenko^a, A.S. Bogomyakov^a, E.M. Zueva^b, I.Yu. Barskaya^a, M.V. Fedin^a, K.Yu. Maryunina^c, E.V. Tretyakov^a, R.Z. Sagdeev^d, V.I. Ovcharenko^{a,*}

^a International Tomography Center, SB RAS, Institutskaya Str. 3A, 630090 Novosibirsk, Russian Federation

^b Kazan National Research Technological University, 68 K. Marx Str., 420015 Kazan, Russian Federation

^c Department of Chemistry, Graduate School of Science, Hiroshima University, 739-8526 Higashi Hiroshima, Japan

^d Kazan Federal University, 18 Kremlyovskaya St., 420008 Kazan, Russian Federation

ARTICLE INFO

Article history:

Received 1 June 2015

Accepted 10 July 2015

Available online 20 July 2015

Keywords:

Spin crossover

Cu(II) complexes

Nitroxides

Phase transitions

Magnetostructural correlations

ABSTRACT

New nitronyl nitroxides L^{Me} and $L^{\text{Me-CP}}$ containing a 4-methylpyridin-3-yl substituent were synthesized. It was found that the interaction of $\text{Cu}(\text{hfac})_2$ with L^{Me} and $L^{\text{Me-CP}}$ gave binuclear $[\text{Cu}(\text{hfac})_2 L^{\text{Me}}]_2$ and $[\text{Cu}(\text{hfac})_2 L^{\text{Me-CP}}]_2 \cdot \text{Solv}$ ($\text{Solv} = n\text{-C}_6\text{H}_{14}$, $n\text{-C}_{10}\text{H}_{22}$, $n\text{-C}_{16}\text{H}_{34}$) and chain polymer $\{[\text{Cu}(\text{hfac})_2 L^{\text{Me}}]_2 [\text{Cu}(\text{hfac})_2]\}_\infty$ heterospin complexes. An important structural peculiarity of L^{Me} and $L^{\text{Me-CP}}$ is a large dihedral angle between the planes of the $\text{O}-\text{N}-\text{C}=\text{N} \rightarrow \text{O}$ paramagnetic fragment and the pyridine ring: 55.2 and 56.1°, respectively. The presence of a methyl group in the pyridine ring of the nitroxide molecule in $\{[\text{Cu}(\text{hfac})_2 L^{\text{Me}}]_2 [\text{Cu}(\text{hfac})_2]\}_\infty$ proved favorable for spin transition at nearly room temperature.

© 2015 Elsevier Ltd. All rights reserved.

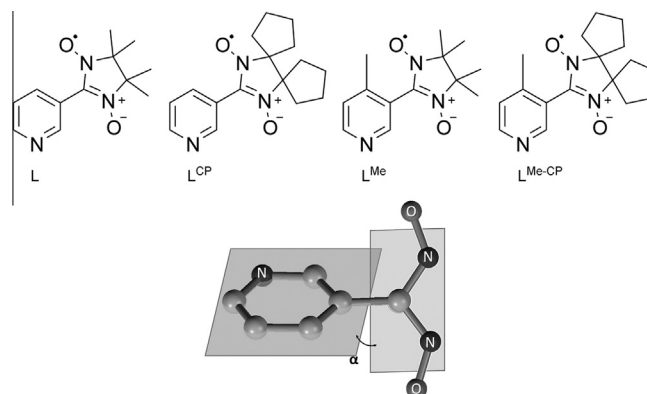
1. Introduction

Breathing crystals based on heterospin complexes of Cu(II) with nitroxides have attracted the attention of researchers as objects in which spin transitions are possible [1–4]. These crystals generally have high mechanical stability and do not decompose during phase transitions. This allows one to perform single crystal to single crystal transformations, i.e., to study the structure of polymorphs using the same single crystal and to compare the structural features of the high- and low-temperature phases with the magnetic characteristics of the compound.

The possibility of varying the structure of the starting organic paramagnetic ligand many times is a valuable peculiarity of compounds from this class. This is an effective tool for changing the characteristics of the observed spin transitions, which proved highly sensitive to the molecular structure of nitroxide [5–8]. This necessitated studies to reveal the relationship between the structural features of the starting nitroxide and the magnetic properties of the heterospin complex.

The goal of this study was to investigate the magnetostructural correlations for $\text{Cu}(\text{hfac})_2$ complexes with nonplanar pyridyl-substituted nitronyl nitroxides, in which the dihedral angle (α) between the $\text{O}-\text{N}-\text{C}=\text{N} \rightarrow \text{O}$ fragment of the 2-imidazoline ring and the pyridine ring bonded with it is reasonably large [9]. To obtain nitroxides with large α , we introduced a methyl group

in the 4-position of the pyridine ring of known nitroxides L [10] and L^{CP} [11] and obtained 2-(4-methylpyridin-3-yl)-4,4,5,5-tetra methyl-4,5-dihydro-1H-imidazole-3-oxide-1-oxyl (L^{Me}) and 2-(4-methylpyridin-3-yl)-4,5-bis(spirocyclopentane)-4,5-dihydro-1H-imidazole-3-oxide-1-oxyl ($L^{\text{Me-CP}}$), respectively.



It was shown that the crystals L are formed by two independent nitroxide molecules that differ in the α angle between the pyridine ring and the $\text{O}-\text{N}-\text{C}=\text{N} \rightarrow \text{O}$ fragment of the 2-imidazoline ring: 52.99 and 35.89° (Table 1). Despite the large difference between these values, it is important that the dihedral angle in molecules

* Corresponding author.

E-mail address: Victor.Ovcharenko@tomo.nsc.ru (V.I. Ovcharenko).